

Control of Spins Using Tailored Oxide Structures

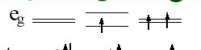
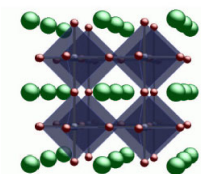
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Motivation: To understand the influence of oxygen concentration and ordering on Co^{3+} spin states.

Approach: Synthesize a controlled range of oxygen contents, δ , in the $\text{NdBaCo}_2\text{O}_{5+\delta}$ system, and survey the structural and magnetic phase diagrams.

Accomplishments: (a) A broad survey of the structural and magnetic properties as a function of δ , and (b) a proposed model of ordered spin-states in the $\delta=0.5$ compound.

Spin States in Co^{3+} Compounds



Jahn-Teller (J-T) Activity

	$t_{2g}^6 e_g^0$	$t_{2g}^5 e_g^1$	$t_{2g}^4 e_g^2$
S	0	1	2
J-T	X	✓	X

The $\text{NdBaCo}_2\text{O}_{5+\delta}$ System

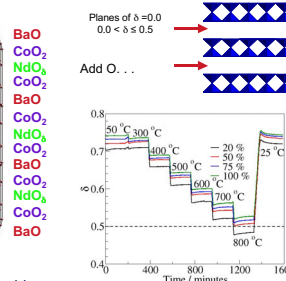
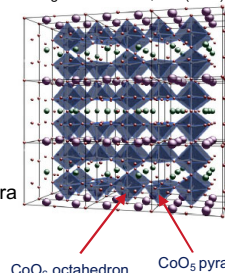
Careful adjustment of T, $p\text{O}_2$ allows control of δ

- Lower symmetry allows coherent J-T

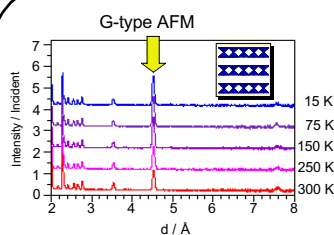
- Tunable mixed-valence -- (Co^{2+} , Co^{3+} , Co^{4+})

- Coordination polyhedra favor different spin states

A. Maignan JSSC 142, 247 (1999)



$\delta = 0$: High Spin, Charge-Disordered

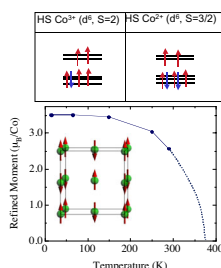


G-type AFM; Refined moment consistent with HS $\text{Co}^{2+}/\text{Co}^{3+}$



96 K

Unlike manganites, *no* evidence for long-range CO
Long-range CO may depend on dimensionality

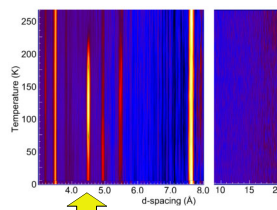


Co-Co Spacing and Charge Order (CO)

YBaCo_2O_5	3.599 Å	CO
$\text{HoBaFe}_2\text{O}_5$	3.566 Å	CO
$\text{NdBaFe}_2\text{O}_5$	3.686 Å	No CO
$\text{NdBaCo}_2\text{O}_5$	3.705 Å	No CO

$\delta = 0.5$: Ordered Spin-State Configuration?

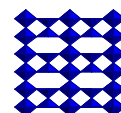
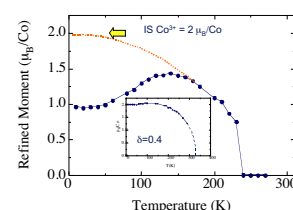
T-dependent neutron diffraction at ISIS



G-type AFM

- Possibility #1: New magnetic phase -- no evidence from NPD

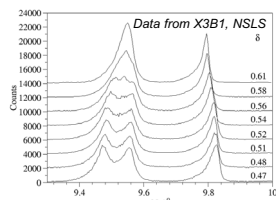
- Possibility #2: Spin-state transition to LS Co^{3+} -- maybe



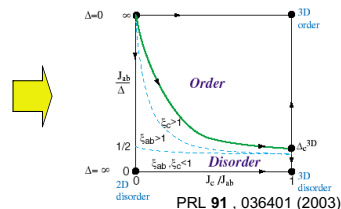
- LS Co^{3+} in octahedra - nonmagnetic
- $S \neq 0$ Co^{3+} in sq. pyramids - magnetic

Future Directions

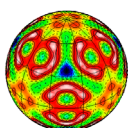
- Detailed synthesis, structural studies at $\delta \sim 0.5$
 - Reproducibly verify spin-state transition/ordering
 - Test how ordered/disordered O sublattice impacts magnetism



- Single Crystal Synthesis for neutron/x-ray scattering:
 - Test Random-Field Ising Model theory of Zachar on charge ordering in $\text{Co}^{2+}/\text{Co}^{3+}$ 2-1-4 compound.
 - Dynamics of spin-state transition



J.C. Burley, J.F. Mitchell, S. Short, D.J. Miller and Y. Tang J. Solid State Chem. 170, 339 (2003)



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